(54) Title: SENSOR ASSEMBLY AND METHOD FOR MEASURING NITROGEN DIOXIDE
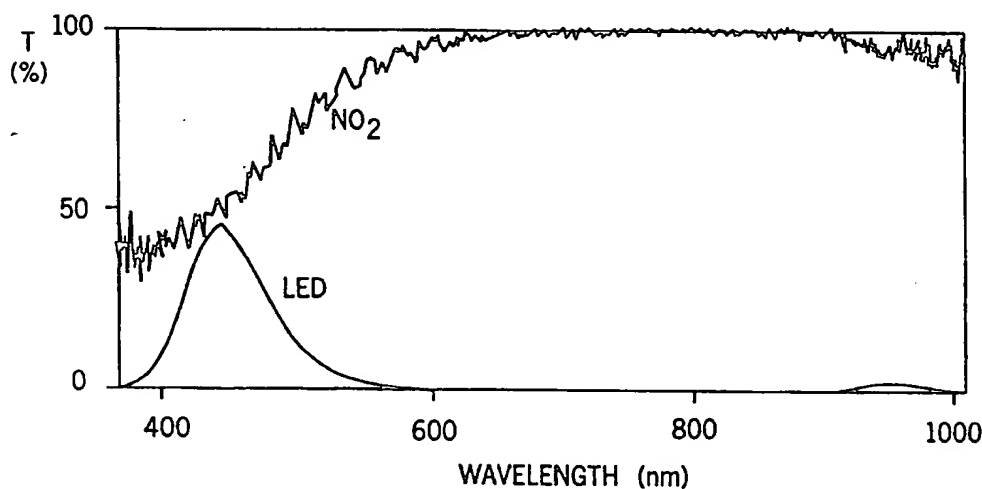
(57) Abstract

A sensing apparatus and method for use in the optical absorption analysis of the NO_2 content of a gas sample. The apparatus and method employ radiation from a semiconductor radiation source. The emission spectrum of the radiation has a maximum wavelength of about 600 nm, preferably 380 – 520 nm. The radiation is passed through the gas sample and sensed by a detector to provide an output signal indicative of the NO_2 content of the gas sample. The sensor apparatus and method may be employed in conjunction with other gas sensing apparatus and methods, such as IR CO_2 measurement or NO sensing.

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SENSOR ASSEMBLY AND METHOD
FOR MEASURING NITROGEN DIOXIDE

BACKGROUND OF THE INVENTION

5   The present invention relates to a sensor assembly and method used for analysis of nitrogen dioxide. The sensor assembly includes a light emitting diode as radiation source, a sample chamber containing the gas to be measured, and at least one radiation detector located to receive the radiation emitted

10   by the radiation source and passed through the gas to be measured. The invention also relates to the analysis of gases containing nitrogen dioxide or nitric oxide.

          The analysis of small concentrations of nitrogen dioxide (NO_2) is typically measured using a sensor for nitric

15   oxide (NO) based on chemiluminescence. The procedure is first to measure the background concentration of NO and then to convert all NO_2 to NO in an oven and after that remeasure the NO content. The difference between the two readings gives an estimation of the concentration of nitrogen dioxide. The method is sensitive

20   to below ppm levels but the measurement cannot be performed reliably in real time especially if the NO background level changes. This is the case when measuring NO delivered to a patient or when measuring the endogenic NO concentration produced in a patient.

25   Nitrogen dioxide is a highly toxic gas often produced from NO in the presence of oxygen. As a precaution, it has therefore been proposed to monitor inhaled NO_2 concentrations to prevent damage to the patient. It is advisable to measure the NO_2 concentration on a breath-to-breath basis, meaning that a

30   response time of about 200 ms is required. This is difficult to meet using a NO_2 to NO converter.

          The same applies for the commonly used electrochemical sensor. It is small and relatively cheap but the response time is too long and the sensitivity low. Such a cell also has a

35   limited lifetime and other gases may interfere with the desired gas measurement. Infrared absorption could also be used to measure NO_2 but the sensitivity is low unless the measuring chamber is very long. A long chamber means increased volume and increased response time. Therefore, this method cannot be used

40   clinically. A good review of all mentioned measuring methods is

found in S.C. Body et al.: Nitric oxide: Delivery, Measurement, and Clinical Application (Journal of Cardiothoracic and Vascular Anaesthesia, Vol. 9, No. 6, 1995: pages 748-763).

It is well known that nitrogen dioxide is one of the few gases that absorbs light in the visible region, see e.g. the reference T.C. Hall, Jr. and F.E. Blacet: Separation of the Absorption Spectra of NO_2 and N_2O_4 in the Range of 2400 - 5000 A (The Journal of Chemical Physics, Vol. 20, No. 11, 1952: pages 1745-1749). To the eye the gas looks brownish in low concentrations. As an aside, it may be noted that this accounts, at least in part, for the brownish color of smog. The gas can even become almost black in high concentrations at elevated temperatures. At room temperature (21°C) the gas is a mixture of the monomeric NO_2 and the dimeric N_2O_4 in equilibrium. About 16% is in form of NO_2. At 100°C this fraction has increased to 90% and at about 120°C practically all molecules are in the monomeric state. Only the monomeric NO_2 absorbs visible light above 400 nm so gas temperature is an important parameter unless the isobestic point at about 350 nm, where both types have similar absorption, can be used. The absorption band is broad and almost continuous between about 300 nm and 600 nm with a region of high absorption without disturbance from N_2O_4 approximately between 390 nm and 450 nm. The absorption can be measured using either a mercury source with emission lines either at 405 nm or 436 nm or a tungsten lamp filtered to give a wavelength band at the blue end of the spectrum. The problem with these measuring systems is that the source is slow which means that it is not possible to utilize the benefits of a system with high frequency modulation. Therefore, these systems, in addition to being quite bulky, power consuming, and complicated, are not suitable for fast measurements of very low concentrations (<1ppm) of nitrogen dioxide. In addition, at least the mercury source has limited lifetime.

In U.S. Patent 4,857,735, a spectrophotometer incorporating at least one light emitting diode is presented for conventional measurement of solutions. The absorption is measured through a short cuvette and the reference signal is obtained from measurement of a blank solution. This means that the measurement, in practice, is slow. A high light intensity is

essential for measuring solutions with sometimes very high absorbances. Therefore high current pulsing with a small duty cycle is important.

However, for gas measurements there is no need for such intensive pulses because the absorption is always small. The high current would produce excessive current noise which would badly disturb the gas measurement and raise the minimum level of detectable gas concentration. Because of the slow measurement, no means for correction of fast drifts are provided and because of the nature of the measurement no means for compensating changes in source intensity or detector sensitivity are present. The instrument as such would consequently not be suitable for measuring gases such as nitrogen dioxide.

BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to provide a sensor assembly and method for the analysis of nitrogen dioxide with a radiation source efficiently emitting light in the blue end of the visible spectrum. A second object of the invention is to provide a sensor assembly, the source of which is modulatable at a frequency that is high compared to changes measurable e.g. in breathing gas. A third object of the invention is the provision of such a sensor assembly, which is both cheap and simple to construct and long-lasting and thus reliable for monitoring of toxic levels of nitrogen dioxide. A fourth object of the invention is to provide such a sensor assembly, which can measure small concentrations of nitrogen dioxide without interference from other gases, especially nitric oxide. A fifth object of the invention is the provision of such a sensor assembly, which in combination with a sensor for nitric oxide, can measure small concentrations of both nitrogen dioxide and nitric oxide in real time. A sixth object of this invention is to provide such a sensor assembly, which in combination with a gas converter, can also indirectly measure nitric oxide.

A salient feature of the sensor assembly according to the invention is that it can be made small, simple, fast, long-lasting, and reliable. The reason for this is that a light radiating diode is used as light source in the sensor assembly. Blue emitting light emitting diodes, commonly known as LEDs, with high enough optical power and long enough lifetime have not been

possible to produce commercially until recently. The emission
spectrum of such a light emitting diode fits well to the
absorption spectrum of nitrogen dioxide which means that all the
benefits of light emitting diodes can be utilized. Since the
5   only gas the sensor assembly reacts to is nitrogen dioxide and
since the sensor assembly does not change the composition of the
measured gas it is possible to made fast measurements of small
concentrations of both nitrogen dioxide and nitric oxide by
combining the sensor assembly with a sensitive and fast sensor
10   for nitric oxide, preferably a sensor based on chemiluminescence.

          Various other features, objects, and advantages of the
invention will be apparent from the following detailed
description and the drawings.

          BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING
15   The invention will be further understood by reference
to the following detailed description taken in conjunction with
the drawing, in which:

          Figure 1 shows a spectrum of nitrogen dioxide in the
visible and near-infrared region together with a typical emission
20   spectrum of a light emitting diode suitable for use in the
present invention;

          Figure 2 shows, in longitudinal section, a sensor
assembly for nitrogen dioxide according to the invention;

          Figure 3 shows an alternative embodiment of a sensor
25   assembly for nitrogen dioxide according to the invention;

          Figure 4 shows an alternative sensor assembly for
nitrogen dioxide according to the invention connected to an
infrared sensor and a sensor for nitric oxide;

          Figure 5 shows a system with an alternative sensor
30   assembly according to the invention connected to be able to
indirectly measure nitric oxide; and

          Figures 6 and 7 show further embodiments of the sensor
assembly according to the invention.

          DETAILED DESCRIPTION OF THE INVENTION
35   As previously mentioned, nitrogen dioxide (NO_2) is one
of the few gases that absorbs visible light. The absorption is
caused by the complex electronic absorption system A^2B_1-X^2A_1 with
superimposed rotational fine structure. The maximum absorption
is approximately at 390 nm, as can be seen in Figure 1, but the

absorption region is broad extending to about 600 nm and even further as a weak absorption. The red end of the spectrum will get more prominent with higher concentration and temperature. For low concentrations only the blue region below about 520 nm
5   shows strong enough absorption to give a reliable measuring result. The concentration of nitrogen dioxide in Figure 1 was in the range of thousand ppm and the measuring length 100 mm. The absorption of nitrogen dioxide has earlier been used for measuring its concentration mainly for laboratory use. As
10   radiation source a mercury lamp is typically used in order to get enough radiant energy in the blue region. Alternatively, a so called UV-VIS spectrophotometer could be applied to measure the absorption spectrum. For environmental purposes a laser or xenon lamp may be used to spectrally scan long paths of small
15   concentrations of nitrogen dioxide in the air, a method called DOAS (Differential Optical Absorption Spectroscopy). The instruments are typically all slow, bulky, expensive, power consuming and not very sensitive for short measuring distances.

            The development of light emitting diodes (LED) has been
20   rapid during the last few years. Until recently it was not possible to manufacture light emitting diodes emitting in the blue region with good enough yield, high enough intensity, and long enough life time. Such a component is now e.g. manufactured by Nichia Chemical Industries Ltd. Of Anan, Japan. The emission
25   spectrum of this LED is also shown in Figure 1 and it can be seen that the spectral features fit those of nitrogen dioxide absorbance very well. Moreover it is possible to take advantage of several features related to the LED when constructing a gas sensor. The LED is a very fast component meaning that high
30   sampling rates can be used. In this way low frequency noise, so called 1/f noise, can be avoided without slowing down the response time. The LED is a very cheap component and it has a very low power consumption with low voltage as opposed to a mercury lamp. It is small size being a semiconductor chip. Thus
35   it is possible to manufacture a small, cheap and sensitive NO_2 sensor with properties surpassing those of earlier measuring devices in many respects.

            The preferred radiation source in this invention is a light emitting diode. However, another possible light radiating

diode to which considerable development efforts are being devoted
is the laser diode. This component resembles a light emitting
diode but is equipped with a resonator making laser action
possible at currents higher than normally needed for good light
5   output from a light emitting diode. The laser diode within the
blue region is still expensive and not very reliable but in the
near future the situation will change. The laser light emission
from such a laser diode has a very narrow spectral bandwidth
compared to the light emission from a light emitting diode. To a
10   slight extent the spectrum of the light emitting diode as shown
in Figure 1 will, however, also be present in the laser diode
spectrum and could be used in a manner similar to what is
described below for the light emitting diode.

A construction of the sensor assembly is shown in
15   Figure 2. The radiation source 1 is a light emitting diode
emitting in the blue region with maximum radiation between about
380 nm and 520 nm depending on the construction of the diode.
The specific LED, the emission spectrum of which is shown in
Figure 1, has its emission maximum at about 450 nm. The LED chip
20   1 in Figure 2 is shown in a typical LED case with a reflector and
a plastic lens that collimates the radiation. Of course it could
be different but the standard package is beneficial because it is
efficient and cheap. It could also be replaced by a laser diode.

The gas to be measured is normally confined to a sample
25   chamber 2 which typically is a long tube with two end windows 3a
and 3b, reflecting inner walls 4 and gas inlet 5a and outlet 5b.
The length of this chamber could be about 100 mm for rapid
measurements of a sampled gas. If the intention is to measure
e.g. breathing gas, a response time of about 200 ms is required
30   in order to resolve all details of the inspiration and
expiration. Of course, the sample chamber could also look
different, e.g. be folded using mirrors, or it could even be
absent for environmental measurements. For a fast sampling
measurement, the sample chamber 2 in Figure 2 is, however, the
35   simplest. A sample chamber is needed especially if the sample
gas is to be measured at a higher temperature than ambient or
temperature stabilization is applied. The benefit of a higher
measuring temperature is not only to prevent condensation of
water on the windows 3 but to get more signal. As pointed out

above, more nitrogen dioxide is formed by conversion from the dimeric form N_2O_4 as temperature rises until all the oxide is in the monomeric form NO_2 at about 120°C. The dimeric form does not absorb in the visible region which means that at higher

5   temperature a deeper absorption and subsequently a better signal and higher sensitivity will result. It is not necessary to heat the sampled gas to 120°C. If heating is applied with a heating element 6 a temperature around 50°C seems adequate for practical reasons. For less sensitive measurements, where the danger of

10   water condensation is absent, heating can be omitted. However, the temperature of the sampled gas must be measured in order to compensate the measured concentration value. In Figure 2 this is done using temperature sensor 7, which preferably could be a thermistor or some other semiconductor component. The foregoing

15   temperature dependence can be stored in memory in a control unit and used for compensation of the total nitrogen dioxide gas concentration according to the measured gas temperature . Other temperature dependencies in the assembly, for example, that of the radiation source and/or that of the detector, may be

20   similarly stored to so as to provide a single temperature dependence function or table for use in the sensor assembly.

     The radiation from an LED 1 of the type described above is quite well collimated. Part of the radiation, 8a goes straight through the sample chamber and the rest, 8b, is

25   reflected off the inner wall 4. The radiation is, in other words, efficiently transmitted through the sample chamber to a detector 9. Even if the LED is preferable because of cost reasons, the radiation transfer would be even simpler using a laser diode because of its beam coherence and the subsequent

30   possibility to collimate the beam very accurately. The detector 9 can preferably be a conventional silicon detector or a so called blue enhanced type of detector, such as that made and sold by United Detector Technology of Hawthorne, CA. Such a component is fast enough to resolve even a high sampling frequency. A

35   sampling frequency of at least about 10 Hz is required for resolving a breathing curve but in this case it is beneficial to work in the kHz range or even higher to avoid 1/f noise. The detector can be connected to a control unit having a narrowband amplifier centered at this high sampling frequency with good

signal-to-noise ratio and good stability as a consequence. An optical filter 10 is positioned in front of the detector 9 to prevent ambient light from disturbing the measurement. Of course the sensor assembly should in practice be built into a light

5   tight case. The filter can be a blue color filter or it can be a narrow band Fabry-Perot filter centered at or near the maximum of the spectral radiation of the LED or laser diode. An accurate measurement is also sensitive to changes in the zero signal, i.e. the signal without absorbing gas. Slow changes can be

10   compensated for by occasionally filling the sample chamber with gas free from NO_2 and measuring and storing this signal for use as a denominator when calculating the gas transmission. This principle does not work for fast changes or in cases when it is not possible to fill the space between the LED source 1 and the

15   detector 9 with non-absorbing gas. There are a number of conventional ways to compensate for such fast changes. If the main source of changes is the LED itself it may be sufficient to monitor its light output using an optical reference detector 11 near the LED as shown in Figure 1. The LED of source 1 is

20   normally connected to a constant current source with a modulation option and the detector 11 can be wired to give feedback to this power source to achieve additional optical stabilization. The so called dark signal is registered when the LED source 1 is in its off state and no light is reaching the detector 9. When both the

25   dark level and zero level are known, the real gas absorption can be calculated and the gas concentration found after linearization and calibration of the sensor assembly. A logarithmic linearization curve is almost correct in this case because Lambert-Beer's law is obeyed as opposed to most infrared gas

30   absorption measurements. However, this fact is of minor importance today when microcomputers can handle any measured linearization function.

It may not be enough to monitor only changes in the LED as shown in Figure 2 or only slow changes in the zero signal.

35   Dirt can accumulate on the windows 3 and walls 4 of sample chamber 2. To compensate for such changes, a reference detector 11 may be provided at the other end of the sample chamber 2 as shown in Figure 3. A beam splitter 12 reflects part of the radiation 8a and 8b on the reference detector 11. An optical

filter 13 in front of the detector 11 has the same function as
filter 10. However, the wavelength region seen by detector 9 and
reference detector 11 must be different so that the signal from
reference detector 11 is not sensitive, or is least less
5   sensitive, to the light absorption in nitrogen dioxide. As it is
beneficial to use the same source 1 for both detectors, the
wavelength region has to be divided. The long wavelength part of
the LED emission, in Figure 1 above about 480 nm, could be used
for detection by reference detector 11. To achieve this, either
10   beam splitter 12 can be dichroic with an edge at about 480 nm, or
filter 13 can be transmissive for wavelengths above the limit if
the beam splitter is conventional. There is still gas absorption
in that region but to a smaller extent than at the maximum of the
LED emission. In other words, the ratio between the measured
15   signal and the reference signal will react to the absorption of
nitrogen dioxide. It is also possible to use the small emission
in the near-infrared region about 950 nm shown in Figure 1 as
reference. Also here a slight gas absorption is observed.
However, the occurrence and strength of this emission depends on
20   the LED manufacturing process and furthermore this wavelength
region does not necessarily reflect the intensity changes at the
blue end of the spectrum because of different absorption
properties of the possible dirt and a fairly strong wavelength
dependence of light scattering.

25   In Figure 4 another embodiment of the sensor assembly
in Figure 3 is shown. Here no beam splitter is used and detector
9 with filter 10 and reference detector 11 with filter 13 are
both positioned side-by-side and optically shielded from each
other. This figure also shows a measuring system for fast
30   measurement of other gases. A measuring system 14 for infrared
absorption is connected in series with the NO_2 sensor assembly
29. In this way it is possible to measure e.g. carbon dioxide.
The sampled gas 15 is drawn into the system using a pump 16.
Normally it is not important which sensor is connected nearer to
35   the sampled gas inlet 15 but sometimes, especially in connection
with breathing gases, it is necessary to have a fastest possible
carbon dioxide signal and this necessitates a position of the
corresponding sensor near the sampled gas inlet 15. In the gas
stream it is often necessary to have a gas drying system 17 to

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avoid water condensation and infrared absorption. A simple solution is to connect a Nafion tube in the sampling line. For establishing a zero level a valve 18 can be turned to an inlet of reference gas 19, normally ambient air, with possible scrubber 20

5   to remove nitrogen dioxide and other disturbing gases, e.g. carbon dioxide CO_2 and nitric dioxide NO.

              Downstream and after the nitrogen dioxide sensor assembly 29 it is possible to connect a sensor 21 for nitric oxide (NO). It can be a conventional electrochemical cell but if

10   small concentrations are to be measured with fast response a chemiluminescent sensor is a better choice. Such instruments are e.g. manufactured by Sievers Instruments, Inc. of Boulder, Colorado as product Model 280. These sensors normally consist of a gas flow restricting element 22 to create underpressure in a

15   reaction chamber 23, an ozone generator 24 with its flow restricting element 25 and a sensitive detector 26, normally a photomultiplier tube. The ozone supplied to the chamber 26 reacts with possible nitric oxide in the sampled gas to form nitrogen dioxide in an excited state and the relaxation creates

20   photons that are detected by detector 26 and are related to the concentration of nitric oxide. Since nitrogen dioxide is formed in sensor 21, this sensor has to be downstream from other sensors. Additionally, the ozone component contaminates and dilutes the sample. A scrubber 27 is normally connected in the

25   sampling line after the nitric oxide sensor to remove ozone and other toxic gases before they are pumped out to the outlet 28 of the system.

              In principle also small concentrations of nitrogen dioxide can be measured using the chemiluminescent sensor 21 if

30   the NO_2 content is first converted to NO by heating. This is the conventional way to measure NO_2 but simultaneous fast measurements of both NO_2 and NO are not possible to perform. First, the NO content must be measured, then the sum of the NO_2 to be measured and converted to NO is measured, and the actual

35   NO_2 concentration is obtained by subtraction. Such a measurement is very vulnerable and apt to changes in e.g. the NO concentration. The measurement is in other words not suitable for real time measurement of e.g. breathing gases. The nitrogen dioxide sensor assembly 29, on the contrary, does not alter the

measured gas in any way and a possible content of nitric oxide
remains intact so that also it can be measured directly using
sensor 21.

5   In Figure 5 another alternative construction of the
nitrogen dioxide sensor assembly is shown. Only one detector 9
is needed because a revolving filter wheel 32 has been used to
alternately position filter 10 and filter 13 in front of the
detector 9. In this way any differences in characteristics that
would arise when two detectors are used are eliminated.
10   Naturally, the revolving speed of filter wheel 32 must be kept
lower than the modulation frequency of the LED.

The system shown in Figure 5 shows like Figure 4
another possibility for connecting the nitrogen dioxide sensor
assembly 29. In addition to being a cheap and reliable sensor
15   for monitoring toxic levels of nitrogen dioxide, according to
Figure 5, it is even possible to indirectly measure nitric oxide
with sensor 29 by first converting the NO content into NO_2 in a
gas mixer 30 e.g. by letting it mix and react with ozone or
oxygen 31. For slow measurements the oxygen in air is adequate
20   for this purpose but for fast measurements ozone can be used.
The embodiment of Figure 5 thus becomes a very cheap and simple
way to monitor, especially, relatively high concentrations of NO
(normally ppm level to a level of a few decades of ppm) e.g. in a
gas container. The NO_2 content, if any, in the sample gas 15 can
25   be measured at first and then the NO content can be found out by
subtracting this NO_2 content from the total amount of NO_2
including the converted NO amount, compensated for the added gas
flow 31 from the gas mixer 30. The difference is the NO content.

Another possibility would be to use the
30   chemiluminescent NO sensor 21 as the mixer and NO converter
instead of mixer 30 shown in Figure 5 and connect it in front of
the NO_2 sensor assembly 29. In this way the NO sensor 21 would
first measure the NO content in the sampled gas, then rapidly
convert it into NO_2 which would be measured by the NO_2 sensor
35   assembly 29, and the actual NO_2 content would be found as the
difference between this total NO_2 content, compensated for the
added ozone gas flow and the NO_2 content resulting from NO
conversion. However the configuration shown in Figure 4 gives a
more direct measurement and it is therefore deemed more reliable

and preferable than the configuration shown in Figure 5.

Figures 6 and 7 present alternative embodiments of the sensor assembly with only one source 1 and one detector 9. Both have a reflecting chopper wheel 33 with a hole in it so that the radiation either goes straight through the sample chamber 2 or is reflected into an alternative reference path on its way to filter 10 and detector 9. In Figure 6 the reference path consists of an optical fiber 34 which transfers the radiation to detector 9. Then it is possible to compensate both for fluctuations in the source radiation and changes in detector sensitivity.

If, in addition, it is necessary to compensate for possible disturbing absorption in the sample gas flow or chamber, a reference chamber 36 can be connected to the sample flow in such a way that any NO_2 content of the sample gas at inlet 15 is removed using a scrubber 38 shown in Figure 7. It would also be possible to connect reference chamber 36 to some other usable gas flow or even use it without gas flow, especially if it could be expected that both chambers 2 and 36 behave similarly when it comes to disturbing absorption. The radiation is directed through reference chamber 36 via mirrors 35 and 37 and using a beam splitter 12. Of course, other optical arrangements are also possible.

Even though many different possibilities have been shown how to use a fast and simple nitrogen dioxide sensor assembly based on a light radiating diode it is evident that many variations of the sensor assembly and many other applications within this invention are possible to construct.

It is recognized that other equivalents, alternatives, and modifications aside from those expressly stated, are possible and within the scope of the appended claims.

CLAIMS

1. A sensor assembly for use in the optical absorption analysis of NO_2 content of a gas sample, said sensor assembly comprising:

5   a semiconductor radiation source emitting radiation having a emission spectrum with a maximum wavelength of about 600 nm;

a sample chamber for containing the gas sample, the NO_2 content of which is to be measured, the radiation from said radiation source passing through said sample chamber; and

10   a detector for receiving the radiation passed through the gas sample in said sample chamber and for providing an output signal indicative of the NO_2 content of the gas sample in said sample chamber.

2. A sensor assembly according to claim 1 wherein said semiconductor radiation source is further defined as emitting radiation having an emission spectrum with a maximum wavelength of about 520 nm.

3. A sensor assembly according to claim 1 wherein said semiconductor radiation source emits radiation in an emission spectrum between about 380 - 520 nm.

4. A sensor assembly according to claim 1 wherein said semiconductor radiation source comprises a light emitting diode.

5. A sensor assembly according to claim 1 wherein said semiconductor radiation source comprises a laser diode.

6. A sensor assembly according to claim 1 further including a further detector for detecting the emitted radiation of said radiation source, said further detector being connected to a power supply for said radiation source for stabilizing the

5   operation of said radiation source.

7. A sensor assembly according to claim 1 wherein said detector comprises a silicon detector.

8. A sensor assembly according to claim 1 wherein said detector comprises a blue enhanced type of detector.

9. A sensor assembly according to claim 1 wherein said detector is coupled to an output signal amplifier.

10. A sensor assembly according to claim 9 wherein said radiation source is operated at a sampling frequency and wherein said output signal amplifier is a narrow bandwidth amplifier, the bandwidth of which is centered at said sampling frequency.

11. A sensor assembly according to claim 1 further including an optical filter interposed in front of said detector along a path of the emitted radiation in said sensor.

12. A sensor assembly according to claim 11 wherein said optical filter passes a spectral band centered on a maximum of the emission spectrum of said radiation source.

13. A sensor assembly according to claim 1 further including a reference detector for detecting the radiation passed through the gas sample in said sample chamber and for compensating said first mentioned detector.

14. A sensor assembly according to claim 13 wherein said reference detector includes means for reducing the sensitivity of said reference detector to spectral absorption resulting from the presence of NO_2 in the gas sample.

15. A sensor assembly according to claim 14 wherein said reducing means comprises means for causing a different spectral region of said emission spectrum to be applied to said reference detector than the spectral region of said emission spectrum applied to said first mentioned detector.

16. A sensor assembly according to claim 15 wherein said means applying different spectral regions of said emission spectrum to said first mentioned detector and said to reference

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detector comprises a dichroic beam splitter interposed in a path
5   of the radiation exiting said sample chamber for applying beams
of different spectral regions to said first mentioned detector
and said reference detector.

17.   A sensor assembly according to claim 15 wherein
said means applying different spectral regions of said emission
spectrum to said first mentioned detector and to said reference
detector comprises filters interposed in front of said first
5   mentioned detector and said reference detector, said filters
passing different spectral regions of said emission spectrum to
said first mentioned detector and said reference detector.

18.   A sensor assembly according to claim 13 wherein
said radiation source emits radiation in a further emission
spectrum and wherein said reference detector detects radiation in
said further emission spectrum.

19.   A sensor assembly according to claim 1 further
including means having a pair of filters, said filters passing
different spectral regions of said emission spectrum and means
for placing one or the other of said filters in front of said
5   detector along a path of the radiation in said sensor for
providing compensation to said detector.

20.   A sensor assembly according to claim 1 further
including a temperature sensor for sensing the temperature of the
gas sample in said sampling chamber and means for compensating
the output signal of said detector in accordance with the sensed
5   temperature of the gas sample.

21.   A sensor assembly according to claim 20 wherein
said sample chamber has a heater operatively associated
therewith.

22.   A sensor assembly according to claim 1 further
including inlet and outlet conduits coupled to said sample
chamber for providing gas flow through said sample chamber, and

wherein an additional gas sensor is located in one of said
5   conduits.

23.   A sensor assembly according to claim 22 wherein
said additional gas sensor comprises an infrared absorption
sensor.

24.   A sensor assembly according to claim 23 wherein
said infrared absorption sensor is located in said inlet conduit.

25.   A sensor assembly according to claim 22 wherein
said additional gas sensor comprises a NO sensor.

26.   A sensor assembly according to claim 25 wherein
said NO sensor is located in said outlet conduit.

27.   A sensor assembly according to claim 25 wherein
said NO sensor is further defined as one capable of measuring
NO_2.

28.   A sensor assembly according to claim 1 further
defined as one for additionally measuring the NO content of the
gas sample, and further including an inlet conduit providing a
gas sample to said sample chamber and wherein said inlet conduit
5   includes a reactor for converting NO in the gas to NO_2 and
wherein said detector includes means for determining the NO
content of the gas from sequential measurements of the NO_2
content of gas samples in said sample chamber.

29.   A sensor assembly according to claim 1 further
defined as one for additionally measuring the NO content of the
gas sample, and further including an inlet conduit for providing
a gas sample to said sample chamber and wherein said inlet
5   conduit includes a reactor, said reactor includes means for
measuring the NO content of said gas sample, said reactor
thereafter converting NO in the gas sample to NO_2, said detector
including means for determining the NO_2 content of the gas sample
from sequential measurement of the NO_2 content of gas samples in
10   said sample chamber.

30. A method for determining the NO_2 content of a gas sample comprising the steps of:

    providing a gas sample;

    passing radiation from a semiconductor radiation source
5   through the gas sample, said radiation having an emission spectrum with a maximum wavelength of about 600 nm; and

    sensing the radiation exiting the gas sample for determining the NO_2 content of the gas sample from the optical spectral absorption characteristics of the sensed radiation
10 resulting from the presence and amount of NO_2 in the gas sample.

    31. The method according to claim 30 further defined as passing radiation having an emission spectrum with a maximum wavelength of about 520 nm.

    32. The method according to claim 30 further defined as passing radiation having an emission spectrum with wavelengths in a range of about 380 - 520 nm.

    33. The method according to claim 30 further defined as passing radiation from a light emitting diode radiation source through the gas sample.

    34. The method according to claim 30 further defined as passing radiation from a laser diode through the gas sample.

    35. The method according to claim 30 further including the step of carrying out a further sensing of the radiation exiting the gas sample and using the results of said further sensing to provide compensation to said first mentioned sensing.

    36. The method according to claim 35 wherein said further sensing is carried out under conditions of reduced sensitivity to spectral absorption resulting from the presence of NO_2 in the gas sample.

    37. The method according to claim 36 wherein said further sensing is carried out using a different spectral region

of the emission spectrum than is employed in said first mentioned sensing.

38.   The method according to claim 36 wherein said further sensing is carried out using a different emission spectrum than is used in said first mentioned sensing.

39.   The method according to claim 30 further defined as sensing the temperature of the gas sample and compensating the sensing results of said sensing step.

40.   The method according to claim 39 further defined as heating the gas sample.

41.   The method according to claim 30 further including the step of carrying out an additional gas sensing procedure on the gas sample.

42.   The method according to claim 41 wherein the further gas sensing procedure is further defined as employing infrared absorption.

43.   The method according to claim 41 wherein the further gas sensing procedure senses NO.

44.   The method according to claim 43 wherein the further gas sensing procedure includes the step of converting NO in the gas sample to NO_2 and wherein the sensing step is further defined as determining the NO content of the gas sample from
5   sequential measurements of the NO_2 content of gas samples.

45.   The method according to claim 41 wherein the further gas sensing procedure measures NO content of the gas sample and converts NO in the gas sample to NO_2, and wherein said sensing step is further defined as determining the NO_2 content of
5   the gas sample from sequential measurements of the NO_2 content of gas samples.
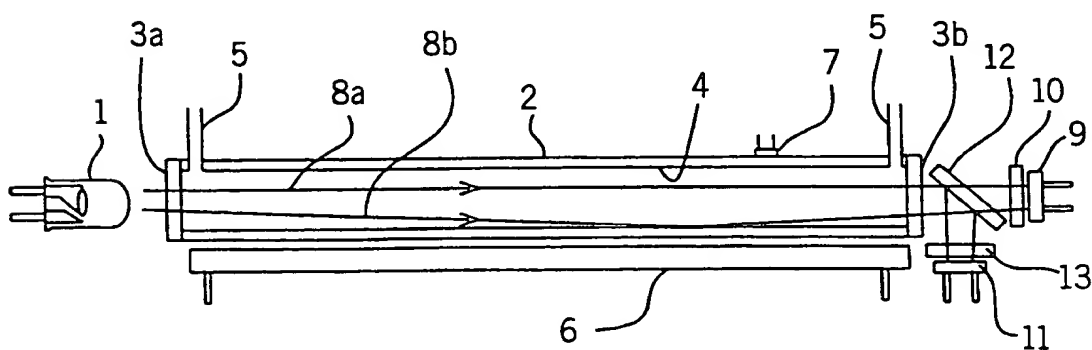
FIG. 1

FIG. 2

FIG. 3

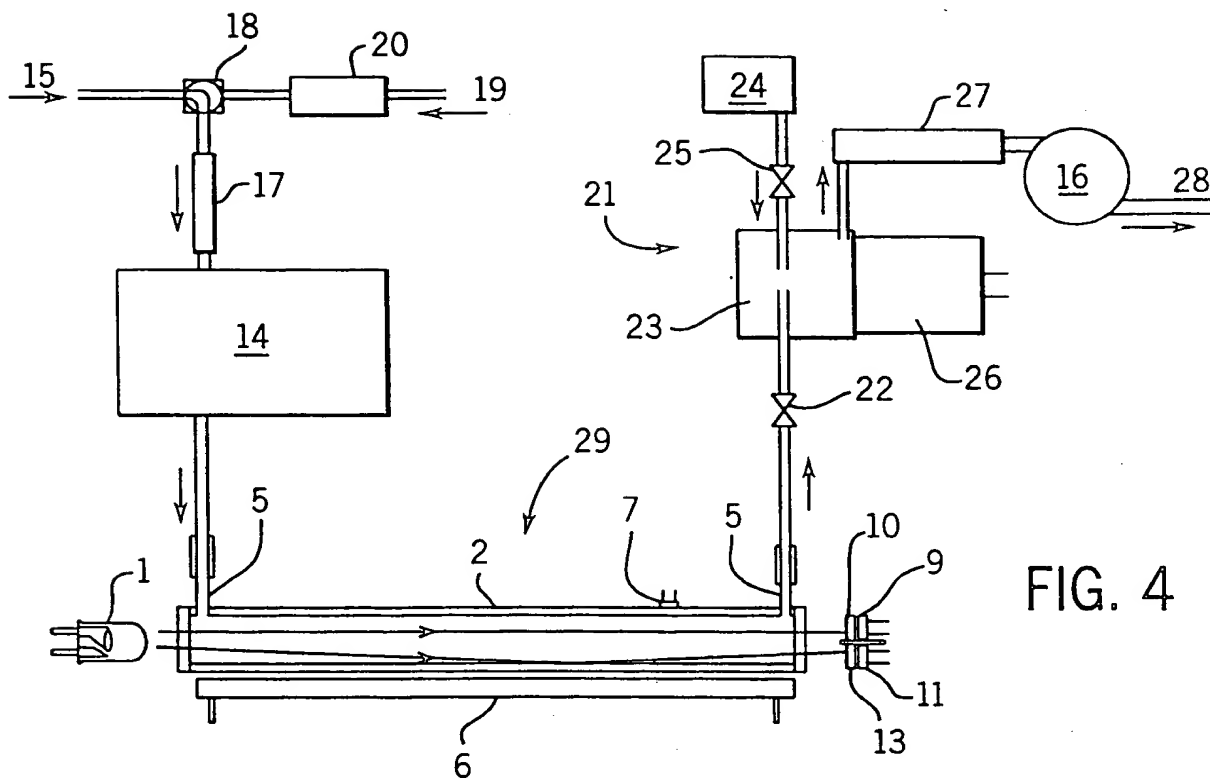FIG. 4

FIG. 5

FIG. 6

FIG. 7
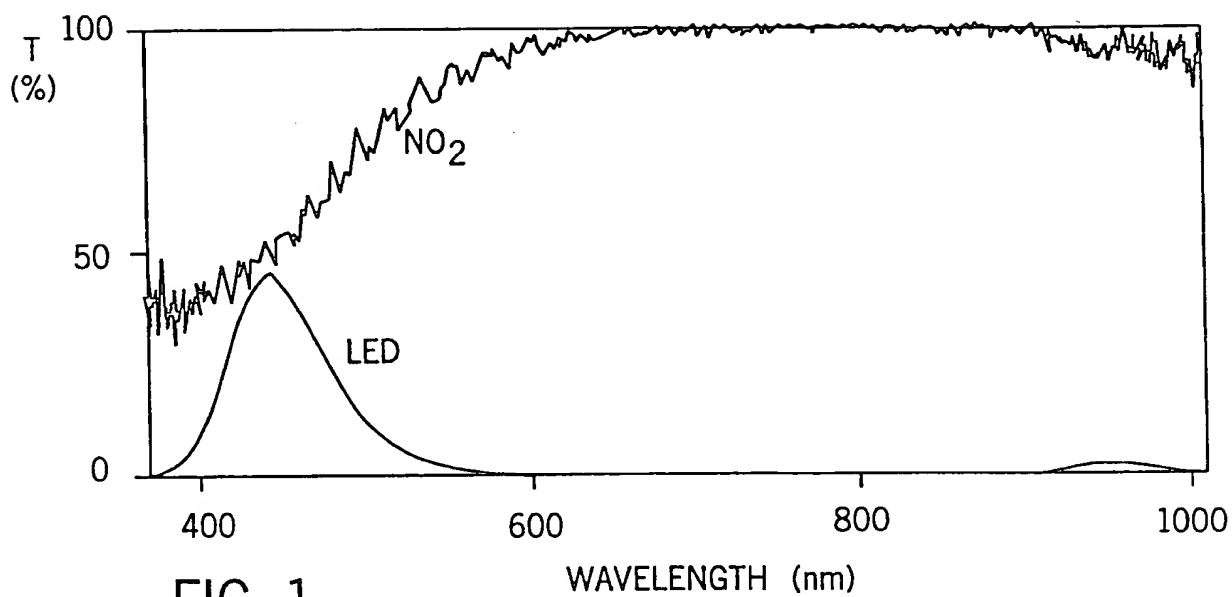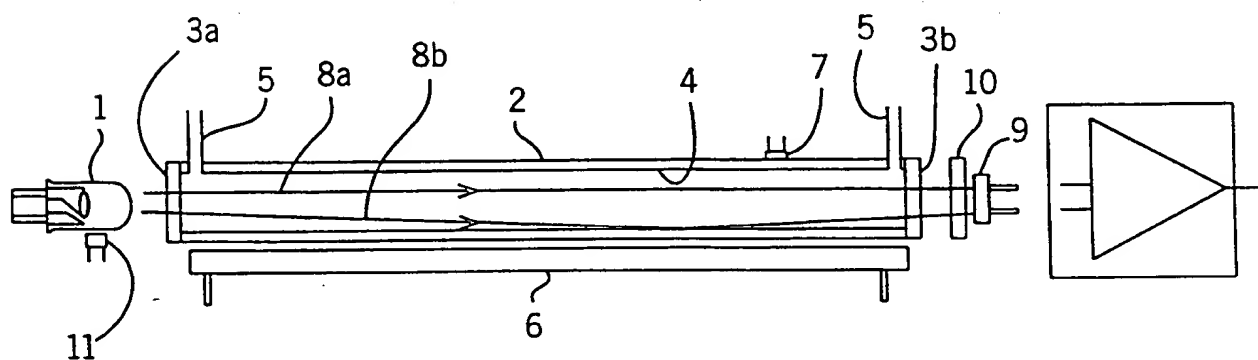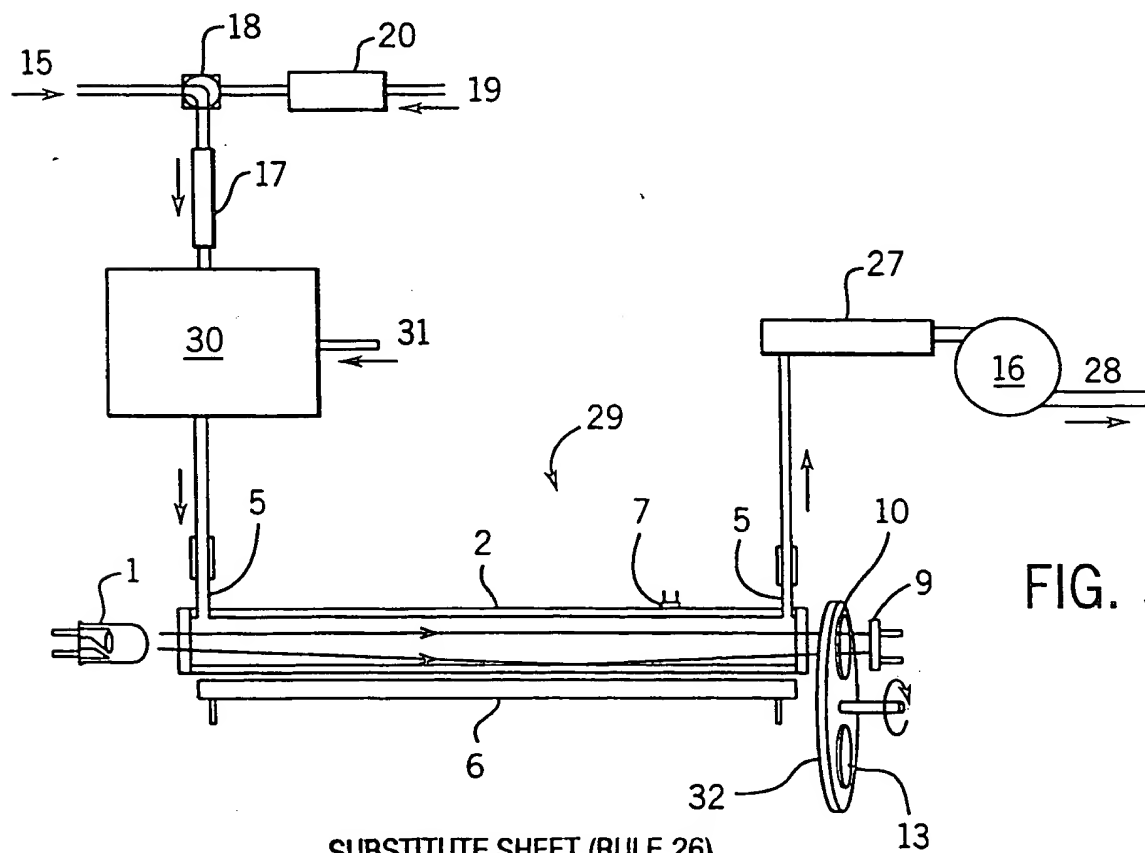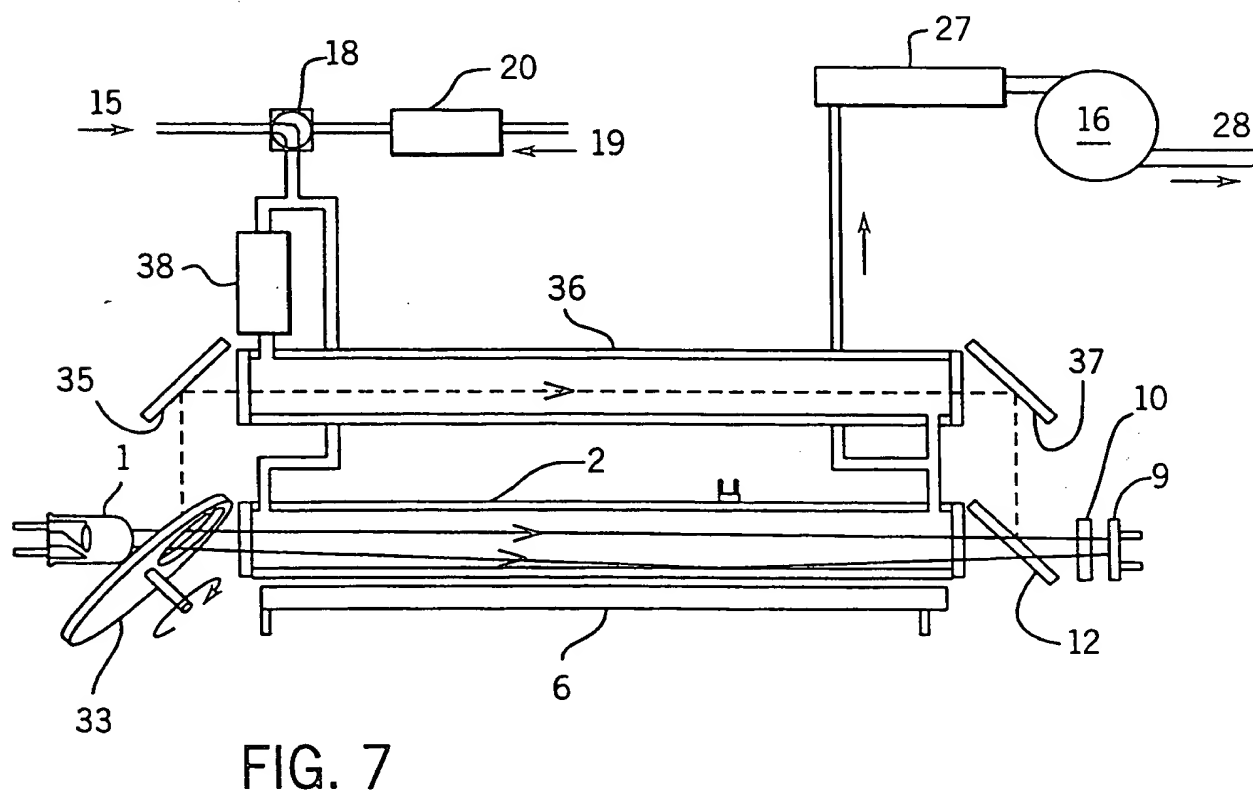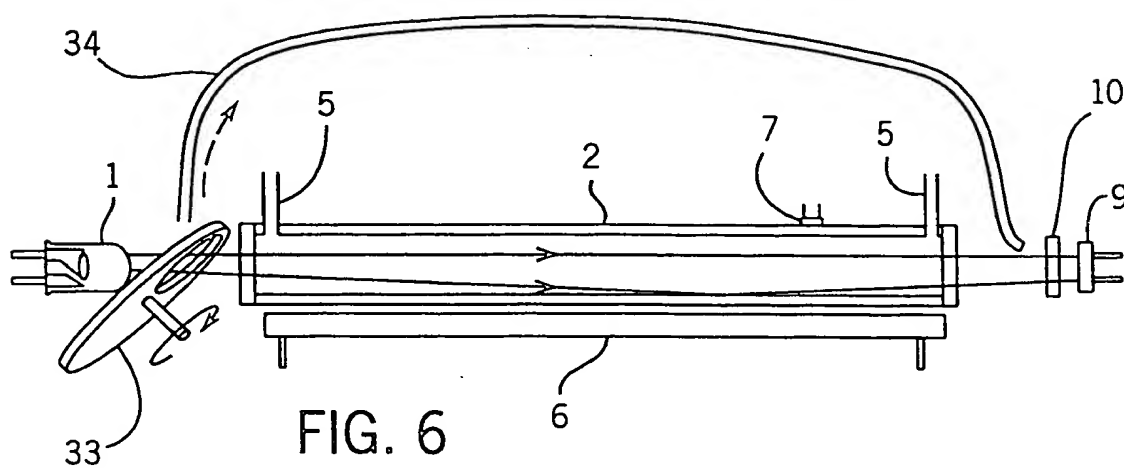
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   G01N21/31   G01J3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   G01N   G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 303 447 A (AMG SYSTEMS LIMITED) 19 February 1997 see page P2, line 8 - line 34 see page 5, line 14 - line 16 see page 3, line 17 - line 28 see page 11; figures 1,5 ---	1-5,7-9, 11-17, 19,30-37
A	DATABASE WPI Section Ch, Week 7913 Derwent Publications Ltd., London, GB; Class E36, AN 79-24361B XP002106208 -& JP 54 021896 A (MITSUBISHI HEAVY IND CO LTD), 19 February 1979 see abstract; figures 1,2 ---	1-3,8, 30-32

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 June 1999	25/06/1999

Name and mailing address of the ISA	Authorized officer
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International Application No

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